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Synthesis of Alkyl-Substituted Tribenzopentaphenes as Versatile Polycondensed Aromatic Hydrocarbon π–π Stacking Building Blocks

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Abstract: We show the versatile synthesis of four tribenzopentaphene derivatives bearing alkyl side chains at three different positions. Substitutions on two of these positions led to subtle intensity changes at the lines of the blue emission, whereas alkylation in the bay region led to dimerization of the pentaphene derivative, resulting in a distortion of the chromophore geometry and an emission shift to green.

Key words: fused-ring systems, cross-coupling, Diels–Alder reaction, cyclodehydrogenation, polycycles

Self-assembled polycondensed aromatic hydrocarbons (PAHs) have drawn much attention in the past two decades because of their remarkable stability and unsurpassed non-covalent π–π stacking[1] bonding, which bestows on them remarkable physicochemical[2] and optoelectronic[3] properties. Considerable experimental effort has been invested in the synthesis of various PAH structures of different shapes and sizes. Nevertheless, most of the synthetic approaches reported to date concentrate on designing highly symmetrical PAH derivatives ranging from linear to disc-shaped,[4] which complicates the decoration of their peripheries with dissimilar pending groups[5] and impedes the π–π stacking.

We present herein the versatile synthesis of a less symmetrical (as compared to hexabenzocoronene, for example) half-lunar-shaped polycondensed aromatic hydrocarbon tribenzo[*fg*,*ij*,*rst*]pentaphene **1** (TBP; Figure 1) carrying solubilizing sidechains in various positions. The convergent synthesis of these compounds requires only a few steps starting from commercially available materials (Scheme 1).

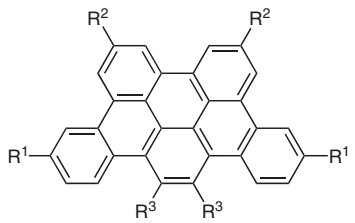

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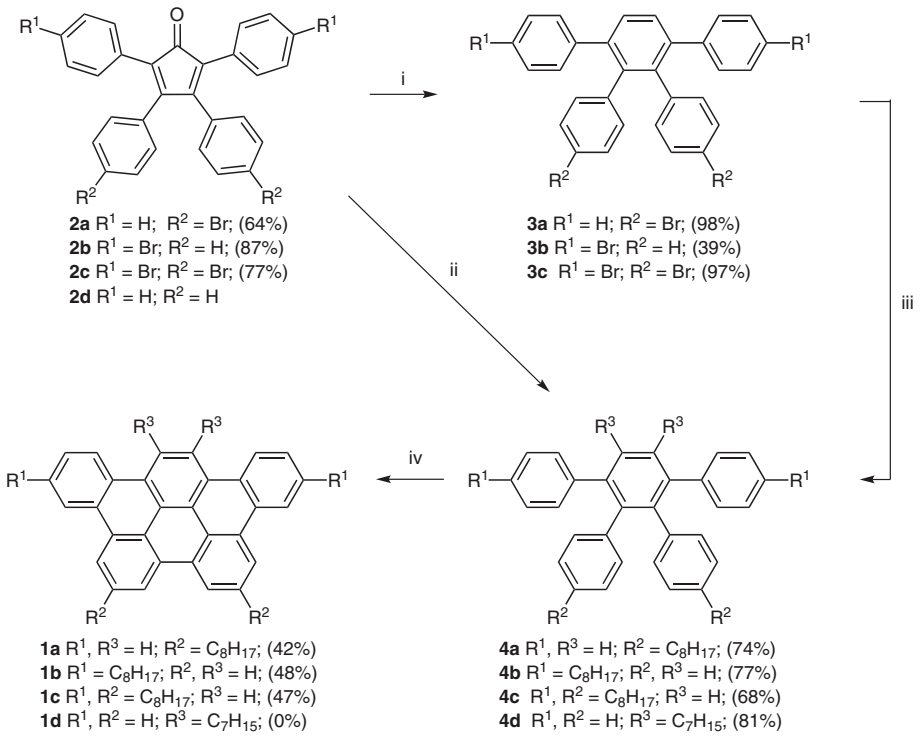
Figure 1 Structure of tribenzo[*fg*,*ij*,*rst*]pentaphene (TBP) **1** indicating the three investigated substitution sites

TBP and variously substituted derivatives had been investigated previously as materials for optoelectronic devices.[6] A TBP derivative substituted in all six positions investigated in this work has been reported but not further investigated.[7] It should be noted that a too dense substitution pattern severely impedes the stacking of the PAH core and thereby reduces the desired π–π interactions. An easy access to specifically substituted TBP derivatives is therefore desirable.

Scheme 1 summarizes the general strategy we adopted[7] to synthesize the TBP derivatives **1a**–**d** bearing pairs of side chains at specific positions. This strategy offers the great advantage of being short and versatile (in view of changing the nature of the side chains), requiring at most four steps starting from commercially available compounds. The reaction steps involve a double Knoevenagel condensation between benzil or 4,4′-dibromobenzil and diphenylpropan-2-one or 1,3-bis(4-bromophenyl)propan-2-one,[8] a Diels–Alder cycloaddition reaction with concomitant CO extrusion, a Kumada cross-coupling,[9] and, finally, a Scholl cyclodehydrogenation reaction, using $FeCl_3$/nitromethane reagent,[10] of the resulting tetraphenylbenzene derivatives **4a**–**d** into the desired PAH target molecules **1a**–**d**. The synthons **2a**–**c** are described elsewhere,[11] and **3b** was generated by carrying out a slightly modified route to that previously reported.[12] The brominated tetraphenylbenzene building blocks **3a**–**c** were synthesized by applying an improved [4+2] Diels–Alder cycloaddition reaction in which acetylene is replaced by the more efficient ethyne source phenylvinylsulfoxide.[13] Attachment of the aliphatic side chains to the aromatic cores were carried out under typical Kumada cross-coupling reaction conditions in which an excess of the aliphatic Grignard reagent was reacted with **3a**–**c** using [Pd(dppf)Cl_2], which afforded **4a**–**c** in good yields. Compound **4d** was finally obtained by reacting tetraphenylcyclopentanone with commercially available 8-hexadecyne in diphenyl ether at reflux.

The delicate final cyclodehydrogenation step was achieved by reacting the synthons **4a**–**d** with anhydrous iron(III) chloride and nitromethane in dichloromethane, affording the desired derivatives **1a**–**c** in acceptable yields. These latter derivatives were purified through a series of precipitation and filtrations on Millipore filters (1 μm pore size). The structures of compounds **1a**–**c** were confirmed by NMR and mass spectrometry analyses.



Scheme 1 Synthesis of pentaphene derivatives. *Reagents and conditions*: (i) phenylvinyl sulfoxide, toluene, reflux, (ii) for **2d**: 8-hexadecyne, diphenyl ether, reflux, (iii) $C_8H_{17}MgBr$, [Pd(dppf)Cl_2·CH_2Cl_2], THF, reflux; (iv) $FeCl_3$, $MeNO_2$, CH_2Cl_2, 45 °C.

Despite numerous attempts, compound **1d** could not be detected in the complex reaction mixture obtained from oxidation of **4d** under standard conditions. Instead, a dimer (*m*/*z* = 1138) was obtained as the major product, which failed to yield resolved NMR spectra, either because of excessive stacking and/or because of paramagnetic impurities [e.g., traces of the abundant oxidant Fe(III)]. When the reaction time and reaction temperature were reduced (i.e., at r.t. for 10 min with $FeCl_3$/nitromethane), the dimeric side product **1e**, CH_2-bridged at the 6,6′-position, was isolated in trace amounts; this compound presumably stems from a double Friedel–Crafts coupling (Figure 2).

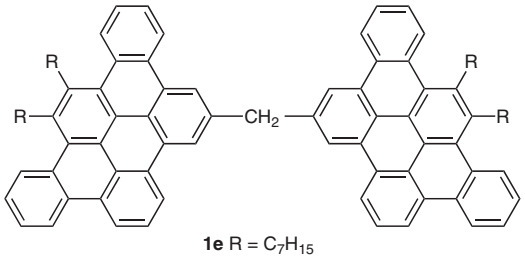
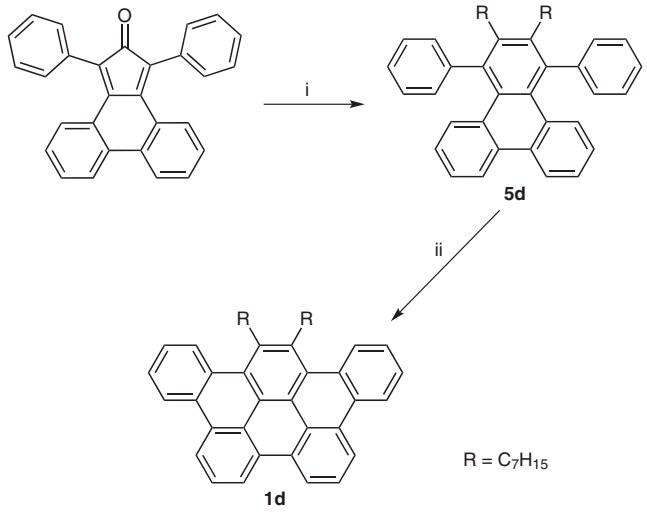


Figure 2 Structure of the 6,6′-CH_2-bridged pentaphene dimer derivative **1e**

In an alternative attempt, we synthesized compound **5d** using an analogous Diels–Alder reaction, to that used to generate **4d** (Scheme 2), but employing the commercially available phencyclone instead of tetracyclone (**2d**). When the Scholl reaction was repeated with **5d**, dimer **1h** (*m*/*z* = 1138) was again isolated as a major product, but this time together with a minor amount of dimer **1f** (*m*/*z* = 1150), as a solid during work-up. In the filtrate, representing about 10% of the total mass, we identified an equimolar mixture of starting material **5d**, the desired compound **1d**, and a dimer **1g** (*m*/*z* =1142). NMR analysis revealed the latter compound to possess the 5,5′-linked dimeric structure shown in Figure 3.



Scheme 2 Synthesis of **1d**: *Reagents and conditions*: (i) 8-hexadecyne, diphenyl ether, reflux, 60%; (ii) $FeCl_3$, $MeNO_2$, CH_2Cl_2, r.t., 10 min, trace (ca. 1%).

We therefore conclude that oxidative dimerization always predominates over intramolecular aryl–aryl coupling, since we observe the completely oxidized dimer **1h** as a

major product even before complete consumption of the starting material. Moreover, the observation of a dimer (m/z = 1150) that corresponds to a singly linked starting molecule, as well as singly linked but fully oxidized dimer (for which a 5,5′-link was deduced from ^{1}H NMR spectrum), permits us to propose a reaction sequence: **5d** → **1f** → **1g** → **1h**, for the major pathway, and: **5d** → **1d**, for the minor pathway. In addition, these findings permit the structure of dimer **1h** to be proposed (Figure 3).

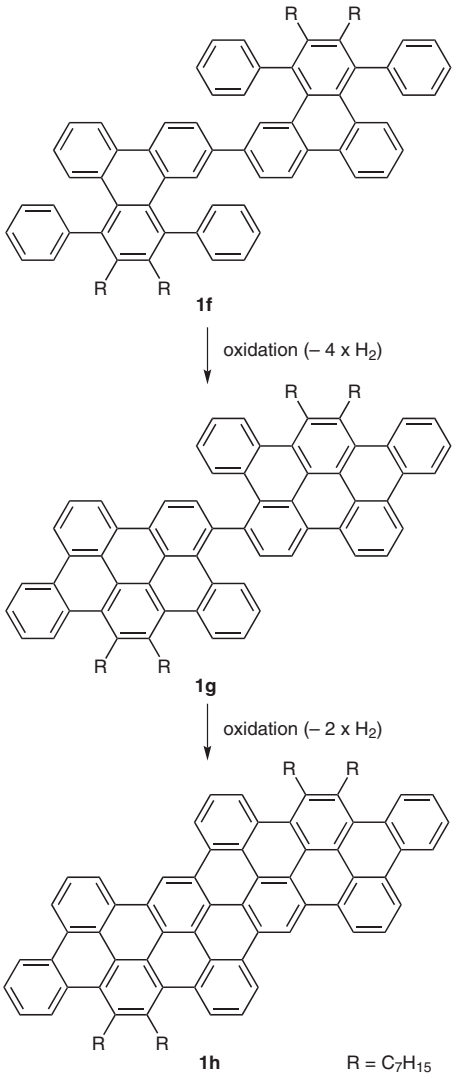


Figure 3 Structures of dimers **1f**–**h**

The TBP derivatives **1a**–**c** show similar UV/Vis absorption spectra, with a strong band at approximately 306 nm and two smaller absorption bands at approximately 355 and 376 nm. They fluoresce in the blue region with similar emission bands (Figure 4).

It is worth noting that the intensities of these bands differ considerably from one derivative to the other, which demonstrates the important influence these lateral substituents exert on the chromophore and on the aggregation behavior of the aromatic core. Due to the reduced symmetry compared to HBC, the 0→0 transition bands for **1a**–**c** gains in

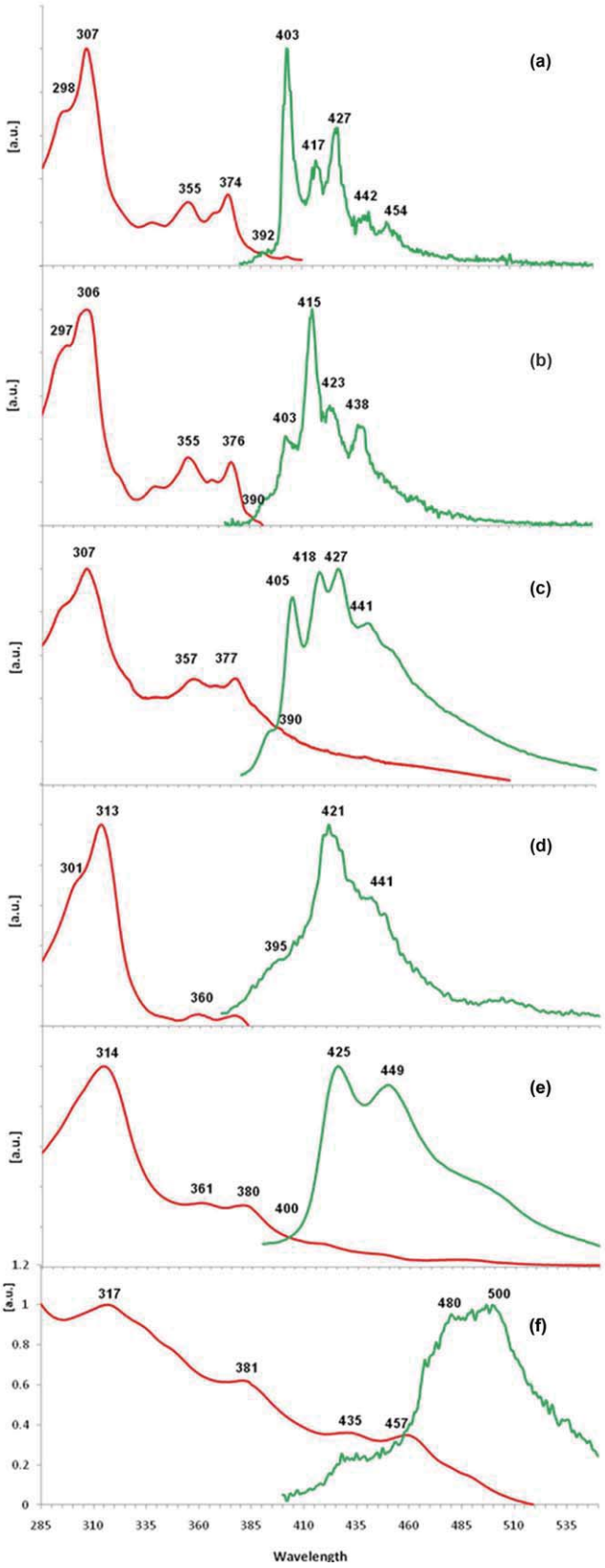


Figure 4 Normalized absorption (red) and emission (green) spectra of the tribenzopentaphene derivatives in toluene: (a) emission (λ_{ex} = 307 nm) of **1a**; (b) emission (λ_{ex} = 306 nm) of **1b**; (c) emission (λ_{ex} = 307 nm) of **1c**; (d) emission (λ_{ex} = 313 nm) of **1d**; (e) emission (λ_{ex} = 314 nm) of **1e**, and (f) emission (λ_{ex} = 317 nm) of **1h**.

intensity and is clearly visible at a similar wavelength for all compounds (ca. 395 nm). As expected, compound **1e** deviates from this scheme; in this case, all transitions are shifted to somewhat longer wavelengths. We attribute this phenomenon to the distorting effect of the substituents. Their location in the bay regions of the molecule forces the TBP core to deviate from planarity, leading to a to contorted sp^2 hybridized manifold, which is known to red-shift the absorption[14a,b] and emission bands (from pale blue to blue-green). Whereas compound **1d** shows UV/Vis and emission spectra that are nearly identical to the CH_2-bridged dimer **1e**, the fully oxidized dimer **1h** shows a very different absorption spectrum and a green emission due to the more extended dibenzo[*fg*,*lm*]dibenzo[5,6:8,9]heptaceno[2,1,18,17,16,15,14-*uvwxyza*$_1$*b*$_1$*c*$_1$*d*$_1$*a*]heptacene core structure.[15]

In conclusion, we show the versatile synthesis of three tribenzopentaphene derivatives substituted at different positions; all of which were obtained in good yields. Emission spectroscopy reveals that alkyl substituents in the examined derivatives **1a**–**c** exert only a very minor influence on the aggregation behavior of the PAH core. Interestingly, intermolecular oxidation products were detected instead of the expected tribenzopentaphene derivative when the alkyl substituents were placed in positions 15 and 16. Thus, the seemingly minor modification in the positions of the alkyl chains has a drastic effect on the reactivity of the tribenzopentaphene derivative, leading to a facile intermolecular Scholl reaction that affords the fully oxidized dimer **1h** even under mild reaction conditions. Further computational work will be carried out to study the influence the alkyl chains have when placed in the aforementioned positions, and which led to polymerization. In contrast to the more symmetrical PAH structures, such as the disc-shaped hexabenzocoronene (HBC), the less symmetrical trapezoidal tribenzopentaphene offers the possibility for more complex functionalization at the periphery without disturbing the π–π stacking of the aromatic core, according to preliminary calculations.

All chemicals were used without further purification as purchased from Acros, Aldrich, Fluka, Merck, Riedel-de-Haën, Strem, or TCI unless otherwise notified. All the reactions were performed under a protective atmosphere using dry nitrogen or argon. The solvents, CH_2Cl_2, Et_2O, pentane, THF, and toluene, were dried and deoxygenated by passage over molecular sieves using a system similar to the that proposed by Grubbs.[16] Column chromatography was carried out with silica gel 60, 0.04–0.06, from either Merck or Brunschwig. Thin-layer chromatography was performed on aluminum sheets coated with silica gel 60 F_{254} and revealed either by UV irradiation or by developing in a solution of $KMnO_4$. Mass spectra were recorded with the following spectrometers: EI spectra were recorded with a HP5988A Quadrupol spectrometer, MALDI-ICR spectra were recorded with a FT/ICR Bruker 4.7 T BioApex II spectrometer. All MALDI spectra used DCTB or TNCQ as matrix with a 337 nm nitrogen laser. NMR spectra were recorded with Bruker Avance DPX 360 MHz (^{1}H: 360 MHz, ^{13}C: 90.55 MHz) and Avance III 500 MHz (^{1}H: 500 MHz, ^{13}C: 126 MHz) spectrometers using $CDCl_3$ as solvent; chemical shifts (δ) are given in ppm, coupling constants (*J*) in Hz, and are referenced to tetramethylsilane (TMS).

2′,3′-Bis(4-bromophenyl)-1,1′:4′,1″-terphenyl (3a)
A mixture of **2a**[11c] (27.45 g, 50.62 mmol) and phenylvinylsulfoxide (11.55 g, 75.93 mmol) in toluene (210 mL) was heated at reflux for 24 h. After cooling to r.t., the mixture was filtered through a short plug of silica gel and the remaining solvents were evaporated in vacuo. The residue was purified by column chromatography (hexanes–EtOAc, 10:1) to give **3a**.

Yield: 25.91 g (98%); white solid.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.50 (s, 2 H), 7.15–7.23 (m, 6 H), 7.03–7.12 (m, 8 H), 6.65 (d, *J* = 8.6 Hz, 4 H).

^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 141.47 (2 C, Ar), 141.17 (2 C, Ar), 138.97 (2 C, Ar), 138.76 (2 C, Ar), 133.22 (4 C, Ar), 130.52 (4 C, Ar), 129.98 (2 C, Ar), 129.95 (4 C, Ar), 127.94 (4 C, Ar), 126.63 (2 C, Ar), 120.30 (2 C, Ar).

MS (EI): *m*/*z* (%) = 540 (100) $[M]^{\cdot+}$.

2′,3′-Bis(4-octylphenyl)-1,1′:4′,1″-terphenyl (4a)
A solution of 1-bromooctane (773 mg, 4.0 mmol) in anhydrous THF (3 mL) was added dropwise to magnesium turnings (100 mg, 4.0 mmol). After complete consumption of the magnesium turnings, the Grignard reagent was added to a mixture of **3a** (540 mg, 1.0 mmol) and [$PdCl_2$(dppf)] (110 mg, 0.15 mmol) in anhydrous THF (7 mL). The resulting mixture was heated at reflux for 24 h. After cooling, the reaction mixture was quenched by addition of MeOH (10 mL), diluted with CH_2Cl_2 (100 mL) and extracted with sat. aq NH_4Cl (30 mL) and H_2O (30 mL). The combined organic layers were dried and the solvent was removed in vacuo. The resulting mixture was separated by column chromatography (pentane–CH_2Cl_2, 1:1) to give the desired product **4a**.

Yield: 450 mg (74%); white powder.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.46 (s, 2 H, ArH), 7.07–7.14 (m, 10 H, PhH), 6.67 (d, *J* = 7.9 Hz, 4 H, ArH), 6.63 (d, *J* = 7.9 Hz, 4 H, ArH), 2.37 (t, *J* = 7.4 Hz, 4 H, Ar-CH_2-C_7H_{15}), 1.35–1.46 (m, 4 H, Ar-CH_2-CH_2-C_6H_{13}), 1.05–1.30 (m, 20 H, Ar-C_2H_4-C_5H_{10}-CH_3), 0.85 (t, *J* = 6.7 Hz, 6 H, Ar-C_7H_{14}-CH_3).

^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 144.21 (2 C, Ar), 141.70 (2 C, Ar), 140.98 (2 C, Ar), 139.21 (2 C, Ar), 139.13 (2 C, Ar), 130.88 (4 C, Ar), 130.44 (4 C, Ar), 129.91 (2 C, Ar), 129.12 (4 C, Ar), 128.08 (4 C, Ar), 126.79 (2 C, Ar), 35.70 (2 C, Ar-*C*H_2-C_7H_{15}), 31.99 (2 C, Ar-C_5H_{10}-*C*H_2-C_2H_5), 31.41 (2 C, Ar-CH_2-*C*H_2-C_6H_{13}), 29.54, 29.41, 29.12 (6 C, Ar-C_2H_4-*C*$_3H_6$-C_3H_7), 22.57 (2 C, Ar-C_6H_{12}-*C*H_2-CH_3), 14.02 (2 C, Ar-C_7H_{14}-*C*H_3).

MS (EI): *m*/*z* (%) = 606.2 (100) $[M]^{\cdot+}$.

6,9-Dioctyltribenzo[*fg,ij,rst*]pentaphene (1a)
To a solution of **4a** (200 mg, 0.33 mmol) in CH_2Cl_2 (20 mL), purged with argon for 20 min, was added a degassed solution of $FeCl_3$ (960 mg, 5.93 mmol, 3 equiv per H to be removed) in $MeNO_2$ (3.5 mL) over 20 min. The reaction medium was heated to 45 °C and bubbled with argon throughout the entire 40 min reaction time (the color turned from slight yellow to green, and finally to brown). The mixture was cooled to r.t., quenched with MeOH (80 mL), and then placed in the refrigerator overnight. The brown precipitate was then filtered several times through a Millipore filter.

The resulting very dark powder was extracted with CH_2Cl_2 and H_2O. The volume of the combined organic layers was reduced to 5 mL and poured over a short silica gel plug using CH_2Cl_2 as eluent to give **1a**.

Yield: 83 mg (42%); orange powder.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.97 (br s, 2 H, ArH), 8.75–8.82 (m, 4 H, ArH), 8.72 (br s, 2 H, ArH), 8.66 (br s, 2 H, ArH), 7.66–7.72 (m, 4 H, ArH), 3.09 (t, *J* = 7.7 Hz, 4 H, Ar-CH_2-C_7H_{15}), 1.93 (quin, *J* = 7.7 Hz, 4 H, Ar-CH_2-CH_2-C_6H_{13}), 1.27–1.59 (m, 20 H, Ar-C_2H_4-C_5H_{10}-CH_3), 0.89 (t, *J* = 6.4 Hz, 6 H, Ar-C_7H_{14}-CH_3).

^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 141.04 (Ar), 130.32 (Ar), 130.14 (Ar), 130.12 (Ar), 129.92 (Ar), 127.44 (Ar), 127.32 (Ar), 127.12 (Ar), 123.81 (Ar), 123.73 (Ar), 123.43 (Ar), 122.93 (Ar), 122.01 (Ar), 121.69 (Ar), 120.56 (Ar), 37.30 (Ar-*C*H_2-C_7H_{15}), 32.44 (Ar-C_5H_{10}-*C*H_2-C_2H_5), 32.10 (Ar-CH_2-*C*H_2-C_6H_{13}), 29.86, 29.81, 29.53 (Ar-C_2H_4-C_3H_6-C_3H_7), 22.86 (Ar-C_6H_{12}-*C*H_2-CH_3), 14.29 (Ar-C_7H_{14}-*C*H_3).

MS (EI): *m*/*z* (%) = 599.9 (100) $[M]^{+\cdot}$.

UV/Vis (CH_2Cl_2, 10^{-5} M): λ_{max} = 298, 306, 355, 374 nm.

Fluorescence (toluene, 10^{-5} M): λ_{max} = 403, 417, 427, 442, 454 (sh) nm.

3′,6′-Bis(4-bromophenyl)-1,1′:2′,1″-terphenyl (3b)
Compound **2b**[11d] (1.3 g, 2.4 mmol) and phenylvinylsulfoxide (547 mg, 3.6 mmol) were dissolved in toluene (10 mL) and heated at reflux under argon for 48 h. After cooling to r.t., the mixture was purified by column chromatography (pentane–CH_2Cl_2, 1:1) to give **3b**.

Yield: 500 mg (39%); white solid.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.46 (s, 2 H, ArH), 7.24–7.32 (m, 6 H, ArH), 6.92–6.99 (m, 8 H, ArH), 6.79 (d, *J* = 8.6 Hz, 4 H, ArH).

^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 140.81 (2 C, Ar), 140.60 (2 C, Ar), 140.12 (2 C, Ar), 139.49 (2 C, Ar), 131.60 (4 C, Ar), 131.53 (4 C, Ar), 130.91 (4 C, Ar), 129.43 (2 C, Ar), 127.31 (4 C, Ar), 126.08 (4 C, Ar), 120.76 (2 C, Ar).

MS (EI): *m*/*z* (%) = 540 (100) $[M]^{+\cdot}$.

3′,6′-Bis(4-octylphenyl)-1,1′:2′,1″-terphenyl (4b)
A solution of 1-bromooctane (428 mg, 2.2 mmol) in anhydrous THF (2 mL) was added dropwise to magnesium turnings (55 mg, 2.2 mmol). After the complete consumption of the magnesium turnings, the Grignard reagent was added to a mixture of **3b**[12] (300 mg, 0.55 mmol) and [$PdCl_2$(dppf)] (61 mg, $8.33\cdot10^{-5}$ mol) in anhydrous THF (4 mL). The resulting mixture was heated at reflux for 24 h. After cooling, the reaction mixture was quenched by addition of MeOH (5 mL), diluted with CH_2Cl_2 (50 mL) and extracted with sat. aq NH_4Cl (20 mL) and H_2O (10 mL). The combined organic layers were dried and the volume was reduced to 5 mL in vacuo and precipitated by addition of EtOH. The product was recrystallized several times (CH_2Cl_2–EtOH) to give **4b**.

Yield: 258 mg (77%); white solid.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.49 (br s, 2 H, ArH), 7.00 (d, *J* = 7.7 Hz, 4 H, ArH), 6.95 (d, *J* = 7.7 Hz, 4 H, ArH), 6.87–6.93 (m, 6 H, ArH), 6.76–6.84 (m, 4 H, ArH), 2.51 (t, *J* = 7.7 Hz, 4 H, Ar-C*H*$_2$-C_7H_{15}), 1.49–1.61 (m, 4 H, Ar-CH_2-C*H*$_2$-C_6H_{13}), 1.18–1.35 (m, 20 H, Ar-C_2H_4-C_5H_{10}-CH_3), 0.88 (*t*, *J* = 6.8 Hz, 6 H, Ar-C_7H_{14}-C*H*$_3$).

^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 140.69 (2 C, Ar), 140.67 (2 C, Ar), 140.24 (2 C, Ar), 140.13 (2 C, Ar), 139.11 (2 C, Ar), 131.59 (4 C, Ar), 129.72 (4 C, Ar), 129.37 (2 C, Ar), 127.52 (4 C, Ar), 126.80 (4 C, Ar), 125.42 (2 C, Ar), 35.49 (2 C, Ar-*C*H_2-C_7H_{15}), 31.87 (2 C, Ar-C_5H_{10}-*C*H_2-C_2H_5), 31.26 (2 C, Ar-CH_2-*C*H_2-C_6H_{13}), 29.45, 29.27, 29.26 (6 C, Ar-C_2H_4-C_3H_6-C_3H_7), 22.68 (2 C, Ar-C_6H_{12}-*C*H_2-CH_3), 14.11 (2 C, Ar-C_7H_{14}-*C*H_3).

MS (MALDI-ICR; DCTB): *m*/*z* (%) = 606.42 (100) $[M]^{+\cdot}$.

3,12-Dioctyltribenzo[*fg,ij,rst*]pentaphene (1b)
To a solution of **4b** (170 mg, 0.28 mmol) in CH_2Cl_2 (20 mL), purged with argon for 30 min, was added a degassed solution of $FeCl_3$ (817 mg, 5.04 mmol, 18 equiv) in $MeNO_2$ (2.5 mL) over 20 min. The reaction medium was heated to 45 °C and bubbled with argon throughout the entire 40 min reaction time (the color turned from slight yellow to green, and finally to opaque brown). The mixture was cooled to r.t., quenched with MeOH (65 mL), and then placed in the refrigerator overnight. The orange-brown suspension was then passed through a Millipore filter several times.

The resulting precipitate was extracted with CH_2Cl_2 and H_2O. The volume of the combined organic layers was reduced to 5 mL and filtered through a short silica gel plug using CH_2Cl_2 as eluent. The volume of the organic layers was reduced and the product was recrystallized several times (CH_2Cl_2–EtOH) and passed through a Millipore filter to give **1b**.

Yield: 80 mg (48%); dark-yellow solid.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 9.11 (s, 2 H, ArH), 9.02 (d, *J* = 7.7 Hz, 2 H, ArH), 8.95 (d, *J* = 7.7 Hz, 2 H, ArH), 8.80 (d, *J* = 8.2 Hz, 2 H, ArH), 8.62 (s, 2 H, ArH), 8.06 (t, *J* = 7.7 Hz, 2 H), 7.60 (d, *J* = 8.2 Hz, 2 H, ArH), 2.94 (t, *J* = 7.7 Hz, 4 H, Ar-C*H*$_2$-C_7H_{15}), 1.78–1.91 (m, 4 H, Ar-CH_2-C*H*$_2$-C_6H_{13}), 1.18–1.67 (m, 20 H, Ar-C_2H_4-C_5H_{10}-CH_3), 0.89 (t, *J* = 6.4 Hz, 6 H, Ar-C_7H_{14}-C*H*$_3$).

^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 142.29 (2 C, Ar), 130.39 (2 C, Ar), 130.08 (2 C, Ar), 130.07 (2 C, Ar), 128.58 (2 C, Ar), 128.27 (2 C, Ar), 127.51 (2 C, Ar), 126.51 (2 C, Ar), 124.89 (2 C, Ar), 123.82 (2 C, Ar), 123.36 (2 C, Ar), 123.20 (2 C, Ar), 121.71 (2 C, Ar), 121.66 (2 C, Ar), 121.02 (2 C, Ar), 36.60 (2 C, Ar-*C*H_2-C_7H_{15}), 32.08 (2 C, Ar-C_5H_{10}-*C*H_2-C_2H_5), 31.90 (2 C, Ar-CH_2-*C*H_2-C_6H_{13}), 29.75, 29.66, 29.48 (6 C, Ar-C_2H_4-C_3H_6-C_3H_7), 22.85 (2 C, Ar-C_6H_{12}-*C*H_2-CH_3), 14.28 (2 C, Ar-C_7H_{14}-*C*H_3).

HRMS (MALDI-ICR; DCTB): *m*/*z* (%) = 402.1390 (13) [M – $(C_7H_{15})_2$], 501.2555 (76) [M – C_7H_{15}], 600.3750 (100) $[M]^{+\cdot}$ (*m*/*z* calcd for $C_{46}H_{48}^{+\cdot}$: 600.37505).

MS (EI): *m*/*z* (%) = 600.2 (100) $[M]^{+\cdot}$, 488.0 (60) [M – C_8H_{16}]$^{+\cdot}$, 376.1 (5) [M – 2 × C_8H_{16}]$^{+\cdot}$.

UV/Vis (CH_2Cl_2, 10^{-5} M): λ_{max} = 297, 306, 355, 376 nm.

Fluorescence (toluene, 10^{-5} M): λ_{max} = 403, 415, 423, 427, 441 (sh) nm.

4,4″-Dibromo-2′,3′-bis(4-bromophenyl)-1,1′:4′,1″-terphenyl (3c)
2,3,4,5-Tetrakis(4-bromophenyl)cyclopenta-2,4-dienone **2c**[11e] (1.44 g, 2.06 mmol) and phenylvinylsulfoxide (407 mL, 470 mg, 1.5 equiv) were dissolved in toluene (10 mL) and heated at reflux under argon for 4 d. After cooling to r.t., the product was purified by column chromatography (pentane–CH_2Cl_2, 1:1) to give **3c**.

Yield: 1.39 g (97%); white powder.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.45 (s, 2 H, ArH), 7.32 (d, *J* = 8.2 Hz, 4 H, ArH), 7.12 (d, *J* = 8.6 Hz, 4 H, ArH), 6.92 (d, *J* = 8.2 Hz, 4 H, ArH), 6.63 (d, *J* = 8.6 Hz, 4 H, ArH).

^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 140.24 (2 C, Ar), 140.23 (2 C, Ar), 130.09 (2 C, Ar), 138.19 (2 C, Ar), 133.04 (4 C, Ar), 131.48 (4 C, Ar), 131.18 (4 C, Ar), 130.80 (4 C, Ar), 129.91 (2 C, Ar), 121.12 (2 C, Ar), 120.67 (2 C, Ar).

MS (EI): *m*/*z* (%) = 697.9 (100) $[M]^{+\cdot}$, 616.9 (5) $[M - Br]^+$, 537.9 (20) [M – Br_2]$^{+\cdot}$.

MS (MALDI-ICR; DCTB): *m*/*z* = 716.79 (100) $[M + Na]^{+\cdot}$.

4,4″-Dioctyl-2′,3′-bis(4-octylphenyl)-1,1′:4′,1″-terphenyl (4c)
A solution of 1-bromooctane (2.12 mL, 3.07 g, 15.9 mmol) in anhydrous THF (50 mL) was added dropwise to magnesium turnings (387 mg, 15.9 mmol). After the complete consumption of the magnesium turnings, the Grignard reagent was added to a mixture of 4,4″-dibromo-3′,4′-bis(4-bromophenyl)-1,1′:2′,1″-terphenyl (**3c**; 1.39 g, 20.0 mmol) and [$PdCl_2$(dppf)] (407 mg, 0.53 mmol, 28 mol%) in anhydrous THF (50 mL). The resulting mixture was heated at reflux for 48 h. After cooling, the reaction mixture was quenched by addition of MeOH (30 mL), diluted with CH_2Cl_2 (300 mL) and extracted with sat. NH_4Cl (80 mL) and H_2O (80 mL). The combined organic layers were dried and reduced to 10 mL and the product was precipitated by adding EtOH. The product was recrystallized several times (CH_2Cl_2–EtOH) to give **4c**.

Yield: 1.12 g (68%); white powder.

^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.47 (s, 2 H, ArH), 6.99 (d, *J* = 7.7 Hz, 4 H, ArH), 6.93 (d, *J* = 7.7 Hz, 4 H, ArH), 6.69 (d, *J* = 8.2 Hz, 4 H, ArH), 6.65 (d, *J* = 8.2 Hz, 4 H, ArH), 2.51 (t, *J* = 8.2 Hz, 4 H, Ar-C*H*$_2$-C_7H_{15}), 2.40 (t, *J* = 8.2 Hz, 4 H, Ar-C*H*$_2$-C_7H_{15}), 1.55 (quin, $^3J_{H-H}$ = 7.3 Hz, 4 H, Ar-CH_2-C*H*$_2$-C_6H_{13}), 1.44 (quin, *J* = 7.3 Hz, 4 H, Ar-CH_2-C*H*$_2$-C_6H_{13}), 1.10–1.35 (m, 40 H, Ar-C_2H_4-C_5H_{10}-CH_3), 0.88 (t, *J* = 7.5 Hz, 12 H, Ar-C_7H_{14}-C*H*$_3$).

^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 140.79 (2 C, Ar), 140.66 (2 C, Ar), 140.61 (2 C, Ar), 139.81 (2 C, Ar), 139.50 (2 C, Ar), 137.51 (2 C, Ar), 131.57 (4 C, Ar), 129.92 (4 C, Ar), 129.29 (2 C, Ar), 127.59 (4 C, Ar), 127.01 (4 C, Ar), 35.69 (2 C, alk), 35.54 (2 C, alk), 32.12 (2 C, alk), 32.07 (2 C, alk), 31.47 (2 C, alk), 31.42 (2 C, alk), 29.68 (2 C, alk), 29.65 (2 C, alk), 29.53 (2 C, alk), 29.46 (2 C, alk), 29.00 (4 C, alk), 22.85 (4 C, Ar-C_6H_{12}-*C*H_2-CH_3), 14.28 (4 C, Ar-C_7H_{14}-*C*H_3).

MS (EI): *m*/*z* (%) = 830.4 (100) $[M]^{+\cdot}$.

3,6,9,12-Tetraoctyltribenzo[*fg,ij,rst*]pentaphene (1c)
To a solution of **4c** (2.00 g, 2.41 mmol) in CH_2Cl_2 (160 mL), purged with argon for 40 min, was added a degassed solution of $FeCl_3$ (7.02 g, 433 mmol, 18 equiv) in $MeNO_2$ (160 mL) over 20 min. The reaction medium was heated to 45 °C and bubbled with argon throughout the entire 2 h reaction time (the color turned from slight-yellow to green, and finally to brown). The mixture was cooled to r.t., quenched with MeOH (550 mL), and then placed in a refrigerator overnight. The orange-brown suspension was then passed through a Millipore filter several times to give **1c**.

Yield: 933 mg (47%); yellow powder.

HRMS (MALDI; DCTB): *m*/*z* (%) = 824.62584 (100) $[M]^{+\cdot}$ (*m*/*z* calcd for $C_{62}H_{80}^{+\cdot}$: 824.62545), 726.52 (20), 627.40 (15), 515.28 (15).

UV/Vis (CH_2Cl_2, 10^{-6} M): λ_{max} = 297, 306, 357, 377 nm.

Fluorescence (toluene, 10^{-5} M): λ_{max} = 405, 418, 427, 441 (sh) nm.

2′,3′-Diheptyl-5′,6′-diphenyl-1,1′:4′,1″-terphenyl (4d)
Commercial tetraphenylcyclopentadienone (1.02 g, 2.6 mmol) and 8-hexadecyne (880 mg, 3.9 mmol, 1.5 equiv) were dissolved in diphenyl ether (22 mL) and heated to 250 °C for 4 d. The reaction mixture turned from dark red to pale yellow as an indication of the evolving reaction.

The diphenyl ether was distilled off in high vacuum (turbomolecular pump) and the resulting mixture was separated by column chromatography (pentane–CH_2Cl_2, 8:2) to give **4d**.

Yield: 2.56 g (81%); white powder.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.14 [app t, *J* = 7.2 Hz, 4 H, Ter, H-C(3,3″, 5,5″)], 7.05–7.10 [m, 6 H, Ter, H-C(2,2″,4,4″,6,6″)], 6.77–6.82 [m, 8 H, Ph, H-C(2,3,5,6)], 6.73–6.77 [m, 2 H, Ter, H-C(4,4″)], 2.51 (app t, *J* = 8.4 Hz, 4 H, Ar-C*H*$_2$-C_6H_{13}), 1.41 (m, 4 H, Ar-CH_2-C*H*$_2$-C_5H_{11}), 1.20 (sext, *J* = 7.2 Hz, 4 H, Ar-C_5H_{10}-C*H*$_2$-CH_3), 1.06–1.15 (m, 12 H, Ar-C_2H_4-C_3H_6-CH_2CH_3), 0.83 (t, *J* = 7.2 Hz, 6 H, Ar-C_6H_{12}-C*H*$_3$).

^{13}C NMR (125.77 MHz, CD_2Cl_2): δ = 141.67 [2 C, Ter, C(1,1″)], 141.56 [2 C, Ph, C(1)], 141.38 [2 C, Ter C(1′,4′)], 139.06 [2 C, Ar, C(5′,6′)], 138.93 [2 C, Ter, C(2′,3′)], 131.67 [4 C, Ph, C(2,6)], 131.05 [4 C, Ter, C(2,2″,6,6″)], 127.46 [4 C, Ter, C(3,3″,5,5″)], 126.65 [4 C, Ph, C(3,5)], 126.16 [2 C, Ter, C(4,4″)], 125.21 [2 C, Ph, C(4)], 32.00 [2 C, Alk, C(5)], 31.51 [2 C, Alk, C(2)], 31.07 [2 C, Alk, C(1)], 30.43 [2 C, Alk, C(3)], 28.95 [2 C, Alk, C(4)], 22.99 [2 C, Alk, C(6)], 14.23 [2 C, Alk, C(7)].

HRMS (MALDI; DCTB): *m*/*z* (%) = 578.39084 (100) $[M]^{+\cdot}$ (*m*/*z* calcd for $C_{44}H_{50}^{+\cdot}$: 578.39070).

6,6′-Bis-15,16-diheptyltribenzo[*fg,ij,rst*]pentaphene (1e)
A solution of **4d** (150 mg, 0.259 mmol) in anhydrous CH_2Cl_2 (45 mL) was degassed with argon for 30 min and $FeCl_3$ (1.232 g, 7.6 mmol, 5 equiv per H to be removed) dissolved in $MeNO_2$ (7 mL) was added dropwise during 30 min at r.t. After 10 min, the reaction was quenched by addition of MeOH (80 mL). The volume of the mixture was reduced to 5 mL and injected with agitation into pentane (100 mL). The precipitate was removed by filtration and centrifugation. After extraction of the remaining solution with EDTA solution (0.1 M, 3 × 50 mL), the organic phase was removed in vacuo and the residue was purified by repeated column chromatography on Alox® (pentane–CH_2Cl_2 gradient).

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.06 (s, 2 H), 8.98 (d, *J* = 8.0 Hz, 2 H), 8.92 (s, 2 H), 8.83 (d, *J* = 7.7 Hz, 2 H), 8.73 (d, *J* = 7.4 Hz, 2 H), 8.72 (d, *J* = 7.4 Hz, 2 H), 8.57 (d, *J* = 7.4 Hz, 2 H), 8.56 (d, *J* = 7.4 Hz, 2 H), 7.96 (t, *J* = 7.8 Hz, 2 H), 7.69 (t, *J* = 7.4 Hz, 2 H), 7.63 (t, *J* = 7.4 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 4 H), 4.89 (s, COSY cross-peak with 9.06, 8.92, 2 H), 3.59 (m, 8 H), 1.52 (m, 8 H), 1.2–1.4 (m, 32 H), 0.88 (t, *J* = 7.0 Hz, 12 H).

HRMS (MALDI; DCTB): *m*/*z* (%) = 401.1326 (95), 499.2414 (53), 585.3543 (89), 1156.6871 (100) $[M]^{+\cdot}$ (*m*/*z* calcd for $C_{89}H_{88}^{+\cdot}$: 1156.68805).

UV/Vis (CH_2Cl_2, 10^{-5} M): λ_{max} = 314, 361, 380, 420 (sh), 448 (sh), 486 nm.

Fluorescence (toluene, 10^{-5} M): λ_{max} = 425, 449, 489 (sh) nm.

2,3-Diheptyl-1,4-diphenyltriphenylene (5d)
Phenylcyclone (260 mg, 0.68 mmol) and 8-hexadecyne (227 mg, 1.02 mmol) were dissolved in diphenyl ether (6 mL) and heated to 250 °C in the absence of light and under an inert atmosphere for 4 d. The diphenyl ether was distilled off and the resulting mixture was separated by column chromatography (pentane–CH_2Cl_2 gradient) to give **5d**.

Yield: 220 mg (60%); white powder.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.37 [ddd, *J* = 8.1, 1.4, 0.6 Hz, 2 H, H-C(8,9)], 7.59 [ddd, *J* = 8.5, 1.3, 0.6 Hz, 2 H, H-C(8,9)], 7.42 [app t, 4 H, H-C(3′,3″,5′,5″)], 7.40 [m, 2 H, H-C(4′,4″)], 7.35 [br. d, 4 H, H-C(2′,2″,6′,6″)], 7.33 [ddd, *J* = 8.1, 7.0, 1.2 Hz, 2 H, H-C(7,10)], 6.98 [ddd, *J* = 8.5, 7.0, 1.4 Hz, 2 H, H-C(6,11)], 2.51 [app t, *J* = 8.4 Hz, 4 H, Ar-C*H*$_2$-C_6H_{13}], 1.41 (m, 4 H, Ar-CH_2-C*H*$_2$-C_5H_{11}), 1.20 (sext, *J* = 7.2 Hz, 4 H, Ar-C_5H_{10}-C*H*$_2$-CH_3), 1.06–1.15 (m, 12 H, Ar-C_2H_4-C_3H_6-CH_2CH_3), 0.83 (t, 6 H, *J* = 7.2 Hz, Ar-C_6H_{12}-C*H*$_3$).

^{13}C NMR (125.77 MHz, CD_2Cl_2): δ = 143.6, 139.2, 137.9, 131.8, 131.2, 130.9, 129.7, 128.5, 126.7, 125.7, 123.0, 32.0, 31.5, 31.1, 30.4, 28.9, 23.0, 14.2.

MS (MALDI; DCTB): *m*/*z* (%) = 576.38 (54) $[M]^{+\cdot}$, 392.16 (100) [M – (C_6H_{13}, C_7H_{15})].

15,16-Diheptyltribenzo[*fg,ij,rst*]pentaphene (1d)
A solution of **5d** (ca. 100 mg, 0.173 mmol) in anhydrous CH_2Cl_2 (45 mL) was degassed with argon during 30 min and $FeCl_3$ (561 mg, 20 equiv, 5 equiv per H to be removed) dissolved in $MeNO_2$ (3 mL) was added dropwise during 30 min at r.t. After 10 min, the reaction was quenched with MeOH (40 mL) and filtered through Millipore. The liquid was evaporated and the brown solid was purified over a silica gel plate (pentane–EtOAc, 9:1) to give **1d**.

Yield: 1 mg (ca. 1%); dark-yellow solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.04 [dd, *J* = 8.5, 0.9 Hz, 2 H, H-C(7,8)], 8.89 [ddd, *J* = 7.9, 0.9, 0.6 Hz, 2 H, H-C(5,10)], 8.78 [ddd, *J* = 8.2, 0.9, 0.5 Hz, 2 H, H-C(4,11)], 8.58 [ddd, *J* = 8.2, 0.9, 0.5 Hz, 2 H, H-C(1,14)], 8.06 (*t*, *J* = 7.9 Hz, 2 H), 7.72 [ddd, *J* = 8.1, 6.9, 1.3 Hz, 2 H, H-C(2,13)], 7.65 [ddd, *J* = 8.1, 6.9, 1.3 Hz, 2 H, H-C(3,12)], 3.59 (m, 4 H), 1.52 (m, 4 H), 1.2–1.4 (m, 16 H), 0.88 (t, *J* = 7.0 Hz, 6 H).

HRMS (MALDI; DCTB): *m*/*z* (%) = 388.13120 (100) [M – (C_6H_{13}, C_7H_{15})], 400.13134 (53), 572.34841 (24) $[M]^{+\cdot}$ (*m*/*z* calcd for $C_{44}H_{44}^{+\cdot}$: 572.34375).

UV/Vis (CH_2Cl_2, 10^{-5} M): λ_{max} = 314, 361, 380, 420 (sh), 448 (sh), 486 nm.

Fluorescence (toluene, 10^{-7} M): λ_{max} = 425, 449, 489 (sh) nm.

10,10′,11,11′-Tetraheptyl-9,9′,12,12′-tetraphenyl-2,2′-bitriphenylene (1f)
Found as a minor impurity in compound **1h**.

MS (MALDI; DCTB): *m*/*z* (%) = 1150.68 (6) $[M]^{+}$, 966.44 (10) [M – (C_6H_{13}, C_7H_{15})], 782.21 (25) [M – (C_6H_{13}, C_7H_{15})$_2$].

15,15′,16,16′-Tetraheptyl-5,5′-bitribenzo[*fg*,*ij*,*rst*]pentaphene (1g)
^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.40 (dd, *J* = 8.2, 1.2 Hz, 2 H), 8.98 (dd, *J* = 7.9, 0.6 Hz, 2 H), 8.89 (dd, *J* = 8.1, 0.6 Hz, 2 H), 8.87 (dd, *J* = 8.5, 0.4 Hz, 2 H), 8.79 (dd, *J* = 8.2, 1.4 Hz, 2 H), 8.61 (dd, *J* = 8.2, 1.2 Hz, 2 H), 8.46 (dd, *J* = 8.0, 1.2 Hz, 2 H), 8.07 (t, *J* = 8.0 Hz, 2 H), 8.06 (d, *J* = 8.5 Hz, 2 H), 7.3 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 2 H), 7.67 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 2 H), 7.64 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 2 H), 7.59 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 2 H), 3.59 (m, 8 H), 1.52 (m, 8 H), 1.2–1.4 (m, 32 H), 0.88 (t, *J* = 7.0 Hz, 12 H).

HRMS (MALDI; DCTB): *m*/*z* (%) = 774.22969 (100) [M – (C_6H_{13}, C_7H_{15})$_2$], 958.44657 (29) [M – (C_6H_{13}, C_7H_{15})], 1142.67510 (55) $[M]^{+}$ (*m*/*z* calcd for $C_{88}H_{86}^{+}$: 1142.67240).

UV/Vis (CH_2Cl_2, 10^{-5} M): λ_{max} = 314, 361, 380, 420 (sh), 448 (sh), 486 nm.

Fluorescence (toluene, 10^{-7} M): λ_{max} = 425, 449, 489 (sh) nm.

3,3′,4,4′-Tetraheptyl-dibenzo[*fg*,*lm*]dibenzo[5,6:8,9]heptacene[2,1,18,17,16,15,14-uvwxyza$_1$b$_1$c$_1$d$_1$a]heptacene (1h)
HRMS (MALDI; DCTB): *m*/*z* (%) = 770.2115 (100) [M – (C_6H_{13}, C_7H_{15})$_2$], 856.3234 (28), 954.4157 (50) [M – (C_6H_{13}, C_7H_{15})], 1138.6415 (92) $[M]^{+}$ (*m*/*z* calcd for $C_{88}H_{82}^{+}$: 1138.64110).

UV/Vis (CH_2Cl_2, 10^{-5} M): λ_{max} = 314, 361, 380, 420 (sh), 448 (sh), 486 nm.

Fluorescence (toluene, 10^{-7} M): λ_{max} = 425, 449, 489 (sh) nm.

References

(1) Grimme, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 3430; and references therein.

(2) (a) Aebischer, O. F.; Aebischer, A.; Donnio, B.; Alameddine, B.; Dadras, M.; Güdel, H.-U.; Guillon, D.; Jenny, T. A. *J. Mater. Chem.* **2007**, *17*, 1262. (b) Wu, J.; Li, J.; Kolbb, U.; Muellen, K. *Chem. Commun.* **2006**, 48. (c) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1340. (d) Alameddine, B.; Aebischer, O. F.; Amrein, W.; Donnio, B.; Deschenaux, R.; Guillon, D.; Savary, C.; Scanu, D.; Scheidegger, O.; Jenny, T. A. *Chem. Mater.* **2005**, *17*, 4798. (e) Bushby, R. J.; Lozman, O. R. *Current Opinion in Colloid & Interface Science* **2002**, *7*, 343. (f) O'Neill, M.; Kelly, S. M. *Adv. Mater. (Weinheim, Ger.)* **2003**, *15*, 1135. (g) Van de Craats, A.; Stutzman, N.; Bunk, O.; Nielsen, M. M.; Watson, M.; Müllen, K.; Chanzy, H. D.; Sirringhaus, H.; Friend, R. H. *Adv. Mater. (Weinheim, Ger.)* **2003**, *15*, 495.

(3) (a) Mori, T.; Kikuzawa, Y.; Takeuchi, H. *Org. Electron.* **2008**, *9*, 328. (b) Hara, T.; Furukawa, K.; Nakamura, T.; Yamamoto, Y.; Kosaka, A.; Jin, W.; Fukushima, T.; Aida, T. *J. Phys. Soc. Jpn.* **2008**, *77*, 34710. (c) Sergeyev, S.; Pisula, W.; Geerts, Y. V. *Chem. Soc. Rev.* **2007**, *36*, 1902. (d) Lloyd, M. T.; Mayer, A. C.; Tayi, A. S.; Bowen, A. M.; Kasen, T. G.; Herman, D. J.; Mourey, D. A.; Anthony, J. E.; Malliaras, G. C. *Org. Electron.* **2006**, *7*, 243. (e) Katz, H. E. *Chem. Mater.* **2004**, *16*, 4748. (f) Moon, H.; Zeis, R.; Borkent, E.-J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322. (g) Xiao, S.; Tang, J.; Beetz, T.; Guo, X.; Tremblay, N.; Siegrist, T.; Zhu, Y.; Steigerwald, M.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 10700. (h) Pisula, W.; Menon, A.; Stepputat, M.; Lieberwirth, I.; Kolb, U.; Tracz, A.; Sirringhaus, H.; Pakula, T.; Muellen, K. *Adv. Mater. (Weinheim, Ger.)* **2005**, *17*, 684. (i) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater. (Weinheim, Ger.)* **2002**, *14*, 99. (j) Schmidt-Mende, L.; Fechtenchötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119. (k) Xiao, S.; Myers, M.; Miao, Q.; Sanaur, S.; Pang, K.; Steigerwald, M.; Nuckolls, C. *Angew. Chem. Int. Ed.* **2005**, *44*, 7390.

(4) (a) Konishi, A.; Hirao, Y.; Nakano, M.; Shimizu, A.; Botek, E.; Champagne, B.; Shiomi, D.; Sato, K.; Takui, T.; Matsumoto, K.; Kurata, H.; Kubo, T. *J. Am. Chem. Soc.* **2010**, *132*, 11021. (b) Fogel, Y.; Zhi, L.; Rouhanipour, A.; Andrienko, D.; Joachim-Raeder, H.; Muellen, K. *Macromolecules* **2009**, *42*, 6878. (c) Feng, X.; Pisula, W.; Ai, M.; Groeper, S.; Rabe, J. P.; Muellen, K. *Chem. Mater.* **2008**, *20*, 1191. (d) Feng, X.; Wu, J.; Ai, M.; Pisula, W.; Zhi, L.; Rabe, J. P.; Muellen, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 3033. (e) Okamoto, T.; Senatore, M. L.; Ling, M.-M.; Mallik, A. B.; Tang, M. L.; Bao, Z. *Adv. Mater. (Weinheim, Ger.)* **2007**, *19*, 3381. (f) Terasawa, N.; Monobe, H.; Kiyohara, K.; Shimizu, Y. *Chem. Lett.* **2003**, *32*, 214. (g) Lee, M.; Kim, J.-W.; Peleshanko, S.; Larson, K.; Yoo, Y.-S.; Vaknin, D.; Markutsya, S.; Tsukruk, V. V. *J. Am. Chem. Soc.* **2002**, *124*, 9121. (h) Yatabe, T.; Harbison, M. A.; Brand, J. D.; Wagner, M.; Müllen, K.; Samori, P.; Rabe, J. P. *J. Mater. Chem.* **2000**, *10*, 1519. (i) Henderson, P.; Ringsdorf, H.; Shuhmacher, P. *Liq. Cryst.* **1995**, *18*, 191.

(5) (a) Feng, X.; Pisula, W.; Takase, M.; Dou, X.; Enkelmann, V.; Wagner, M.; Ding, N.; Muellen, K. *Chem. Mater.* **2008**, *20*, 2872. (b) Chih-Wei, C.; Hong-Yi, C.; Shern-Long, L.; I-Jui, H.; Jey-Jau, L.; Chun-hsien, C.; Tien-Yau, L. *Macromolecules* **2010**, *43*, 8741.

(6) (a) Fujiyama, T.; Toya, Y.; Nakatsuka, M. *Jpn. Kokai Tokkyo Koho* JP 2008098357, **2008**. (b) Nakatsuka, M.; Shimamura, T.; Ishida, T.; Totani, Y. *Jpn. Kokai Tokkyo Koho* JP 2002359081, **2002**.

(7) (a) Doetz, F.; Brand, J. D.; Ito, S.; Gherghel, L.; Müllen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7707. (b) O'Brien, M.; Denton, R.; Ley, S. V. *Synthesis* **2011**, 1157. (c) Ullah, I.; Nawaz, M.; Villinger, A.; Langer, P. *Synlett* **2011**, 1895.

(8) Sauriat-Dorizon, H.; Maris, T.; Wuest, J. D.; Enright, G. D. *J. Org. Chem.* **2003**, *68*, 240.

(9) (a) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higushi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158. (b) Bringmann, S.; Ahmed, S. A.; Hartmann, R.; Mattay, J. *Synthesis* **2011**, 2291.

(10) Kovacic, P.; Koch, F. W. *J. Org. Chem.* **1963**, *28*, 1864.

(11) (a) Zaugg, H.; Rapala, R. T.; Leffler, M. T. *J. Am. Chem. Soc.* **1948**, *70*, 3224. (b) Yeo, S.-J.; Kim, Y.-H.; Lee, D.-H.; Jang, H.-Y.; Hong, S.-K.; Kim, K.-K.; Jeong, D.-S. *PCT Int. Appl.* WO 2007105884, **2007**. (c) Maly, K. E.; Gagnon, E.; Maris, T.; Wuest, J. D. *J. Am. Chem. Soc.* **2007**, *129*, 4306. (d) Vives, G.; Rapenne, G. *Tetrahedron Lett.* **2006**, *47*, 8741. (e) Watanabe, S.; Kido, J. *Chem. Lett.* **2007**, *36*, 590.

(12) Liaw, B. R.; Huang, W. Y.; Huang, P. T.; Chang, M. Y.; Han, Y. K. *Polymer* **2007**, *48*, 7087.

(13) Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597.

(14) (a) Kastler, M.; Pisula, W.; Wasserfallen, D.; Pakula, T.; Muellen, K. *J. Am. Chem. Soc.* **2005**, *127*, 4286. (b) Harris, K. D.; Xiao, S.; Lee, C. Y.; Strano, M. S.; Nuckolls, C.; Blanchet, G. *J. Phys. Chem. C* **2007**, *111*, 17947.

(15) Ray, Dias. J. *THEOCHEM* **1989**, *54*, 57.

(16) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.